Sunshine to Petrol: Reimagining Transportation Fuels

Sandia National Laboratories

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Drivers of Transportation Fuel R&D

The Problem

- **U.S. Petroleum Demand is 20.7 mb/d (2007).**
- **An additional 64 mb/d of petroleum – six times the current capacity of Saudi Arabia – will be needed in the U.S. by 2030.**
- **1 in 8 casualties in Iraq were protecting fuel convoys**

The Solution

- **Policy:**
  - **The Renewable Fuel Standard (RFS) and RFS2 of 2005 and 2007**
- **Targets:**
  - **36 bg/yr renewable fuels by 2022**
  - **15 bg/yr of corn ethanol by 2015**
  - **21 bg/yr from second and third generation cellulosic- or algae-based fuels**
- **Investments:**
  - **FY2008-FY20011: DOE/EERE/BETO, DOE/SC/OBER) $1B in Bioenergy Research Centers, Algae Biofuels Consortia, and Industry-Led Biorefineries**
  - **FY2012: EERE/BETO $195M ($270M FY13 request); SC/OBER $113M**
  - **USDA loan guarantee program.**

A Diversified Policy and R&D Portfolio in Needed

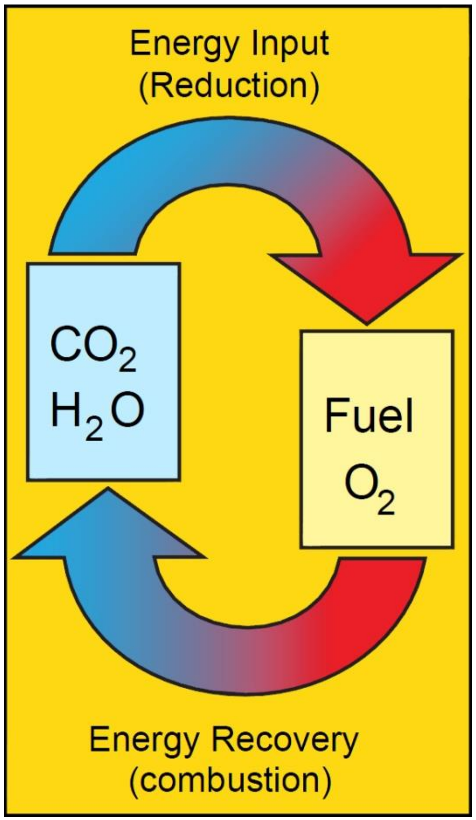
Potential Solutions

- **Natural Gas Reforming (GTL)**
- **Hybrid, Plug-in Hybrid, Electric Vehicles**
- **Biofuels**
- **Solar Fuels (** H_2**,** H_2 **& CO)**

Technology Options

- **Solar Thermochemical**
- **Solar Electrolysis**
- **Photoelectrochemical (PEC)**
- **Photocatalysis**
- **Artificial Photosynthesis**

Solar ThermoChemical Fuels: Sunshine to Petrol (S2P)



Liquid hydrocarbons are the “Gold Standard” for transportation fuels.

S2P: Use the heat of the sun to “energize” CO_2 and H_2O into syngas, a precursor to hydrocarbon fuels.

$$\text{Sunlight} + CO_2 + H_2O \rightarrow \text{Fuel} + O_2$$

<u>H_2O, CO_2 Splitting</u>

$H_2O + \text{energy} \rightarrow H_2 + \frac{1}{2} O_2$

$CO_2 + \text{energy} \rightarrow CO + \frac{1}{2} O_2$

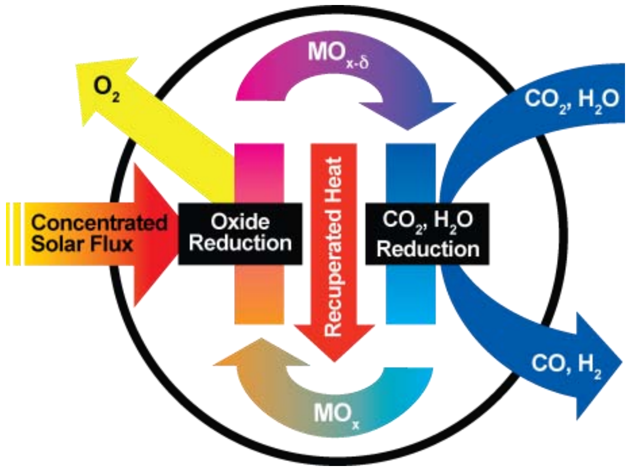
<u>Fischer-Tropsch</u>

$nCO + (2n+1)H_2 \rightarrow C_nH_{2n+2} + nH_2O$

Our Solar Thermochemical Process is Conceptually Simple

$$1/\delta\ MO_x \rightarrow 1/\delta\ MO_{(x-\delta)} + ½\ O_2$$

$$Fe_3O_4 \rightarrow 3\ FeO + ½\ O_2$$



$$1/\delta\ MO_{(x-\delta)} + CO_2 \rightarrow 1/\delta\ MO_x + CO$$

$$3\ FeO + CO_2 \rightarrow Fe_3O_4 + CO$$

R&D focus on:

- **Reactor/Engine**
  - **Maximizing Energy usage (continuous operation, sensible energy recovery i.e. recuperation)**
  - **Interfacing Solar with chemistry**
  - **Minimal parasitic work input**
  - **Decoupling steps (products, conditions, rates)**
- **Catalysts**
  - **Thermodynamics**
  - **Kinetics**
  - **Durability**
- **Systems**
  - **Setting targets, process optimization , economics, life cycle impacts etc.**

We envision new domestic industries in engines, catalysts, and fuels.

Sandia has invested nearly $20M and built an interdisciplinary team.

Principal Investigator – James E. Miller
Project Manager – Tony Martino

Engines

- Solar Reactor - Rich Diver, Tim Moss, Scott Korey, Nathan Siegel
- Reactive Structures - Nathan Siegel, Terry Garino, Nelson Bell, Rich Diver, Brian Ehrhart
- Detailed Reactor Models - Roy Hogan, Ken Chen, Spencer Grange, Siri Khalsa, Darryl James (TTU), Luke Mayer (student)

Catalysts

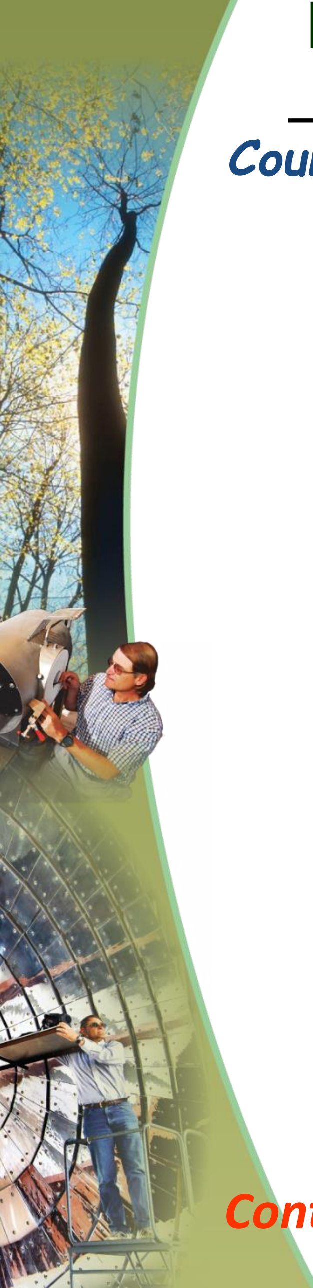
- Reactive Materials Characterization & Development - Andrea Ambrosini, Eric Coker, Mark Rodriguez, Lindsey Evans, Stephanie Carroll, Tony Ohlhausen, William Chueh
- Bulk Transport & Surface Reactions - Gary Kellogg, Ivan Ermanoski, Taisuke Ohta, Randy Creighton
- Thermodynamics & Reaction Kinetics - Mark Allendorf, Tony McDaniel, Chris Wolverton (Northwestern University), Bryce Meredig (student), Heine Hansen (PD), Asegun Henry, Al Weimer (CU), Jon Scheffe (student)

Systems Analysis

- Terry Johnson, Chad Staiger, Christos Maravelias (U-WI), Carlos Henao (student,) Jiyong Kim (PD), Daniel Dedrick

Over 20 conference proceedings, 80 conference presentations, 20 peer-reviewed journal articles, 4 book chapters, and 8 patents

Sunshine to Petrol



The CR5 is our First Engine Prototype

Counter-Rotating-Ring Receiver/Reactor/Recuperator (CR5)

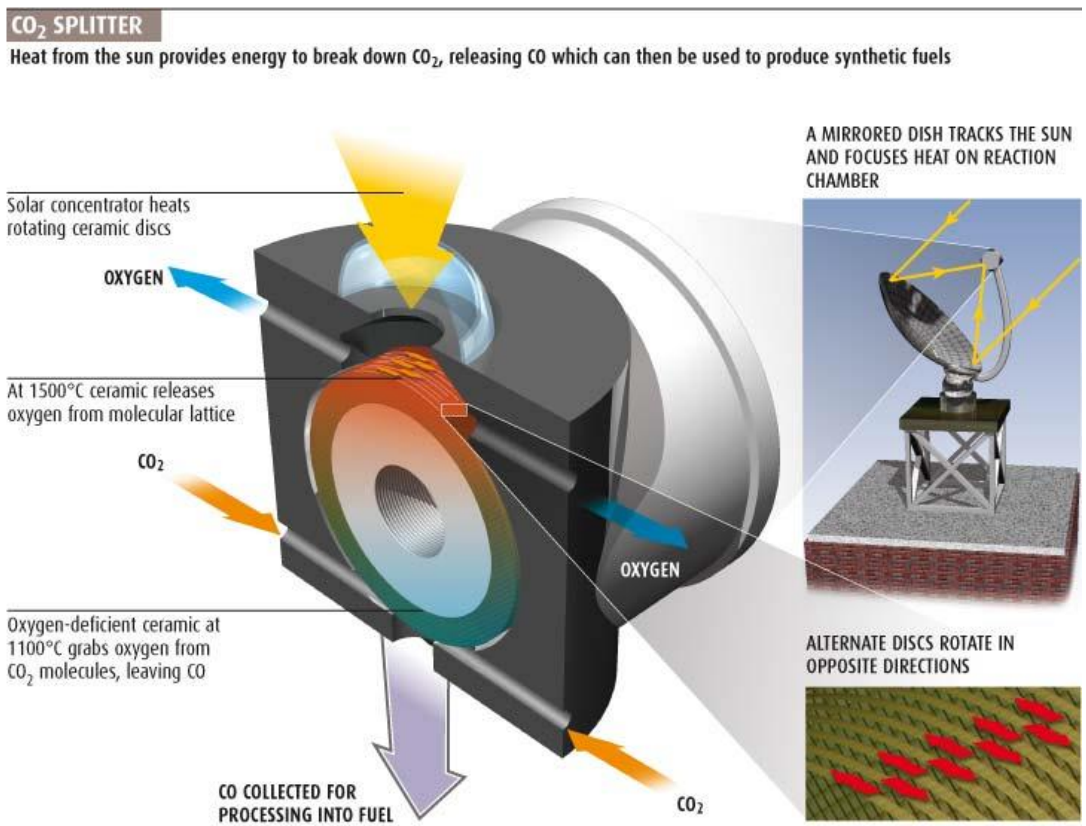


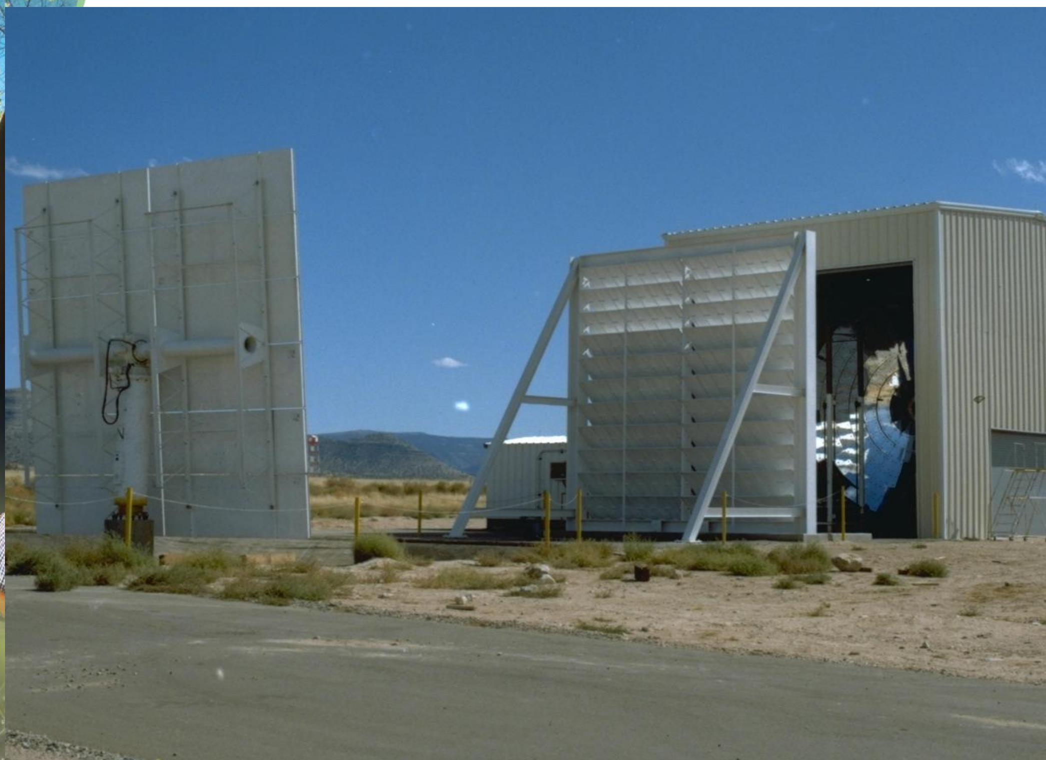
Figure Credit: Popular Science

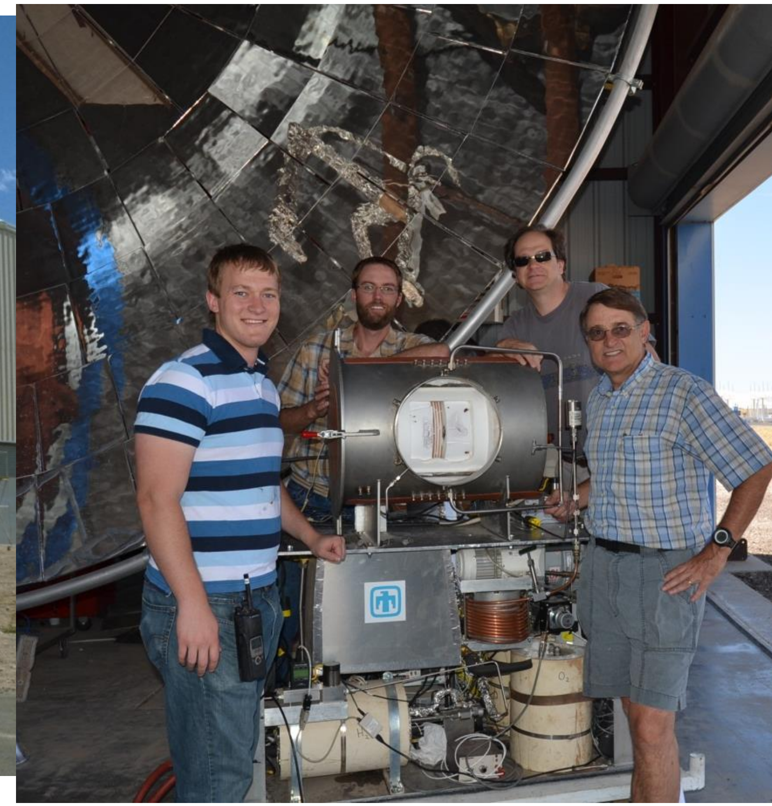
"Reactorizing a Countercurrent Recuperator"

Continuous flow, Spatial separation of products, Thermal recuperation

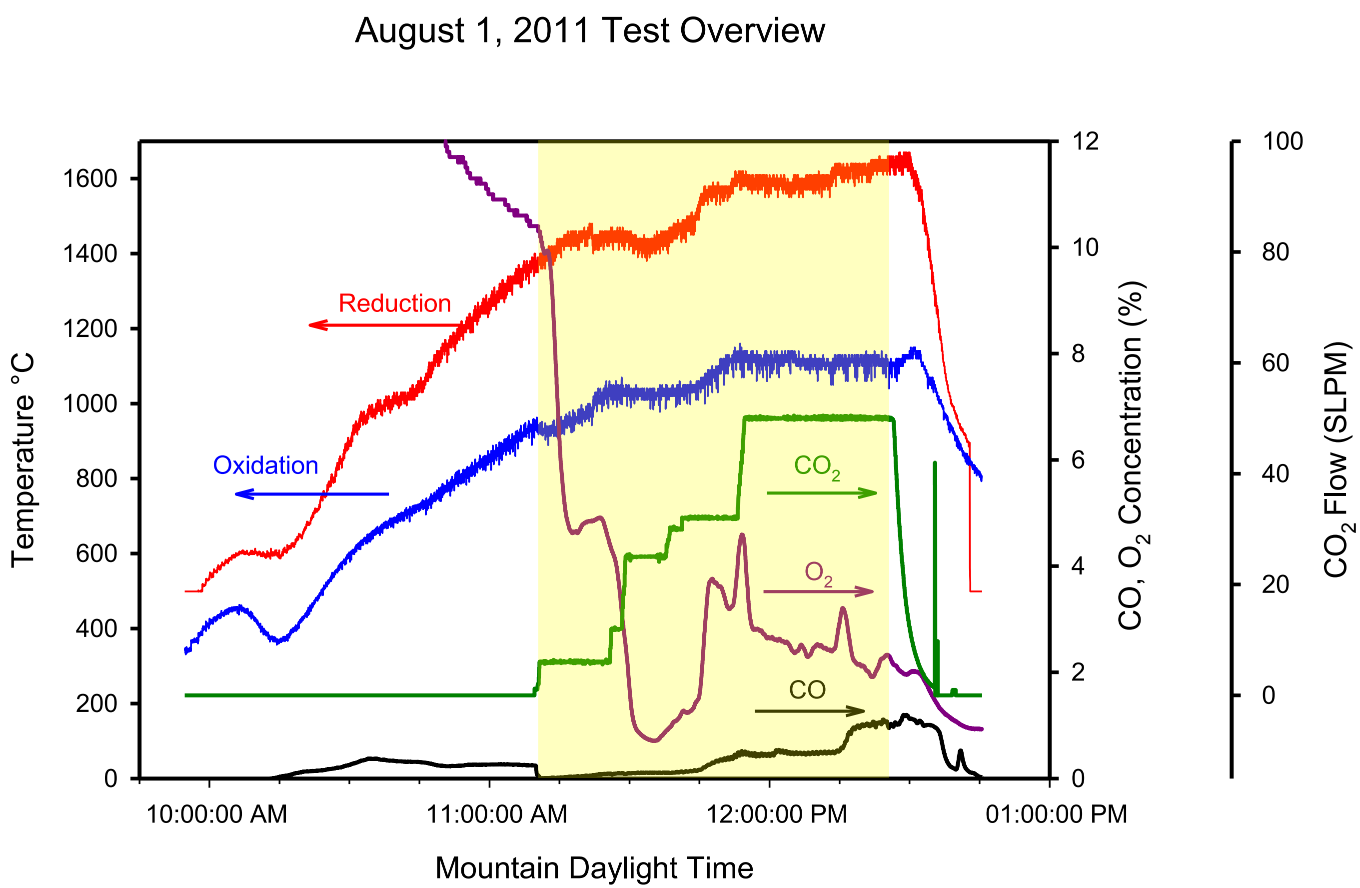
Sunshine to Petrol

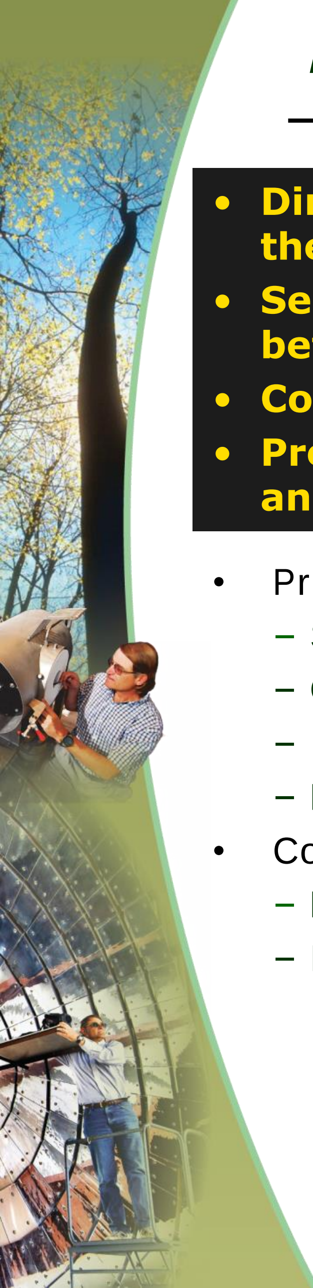
S2P uses concentrated solar power focused on a solar furnace.





This 12-ring test set the standard for heat-to-chemical conversion efficiency.

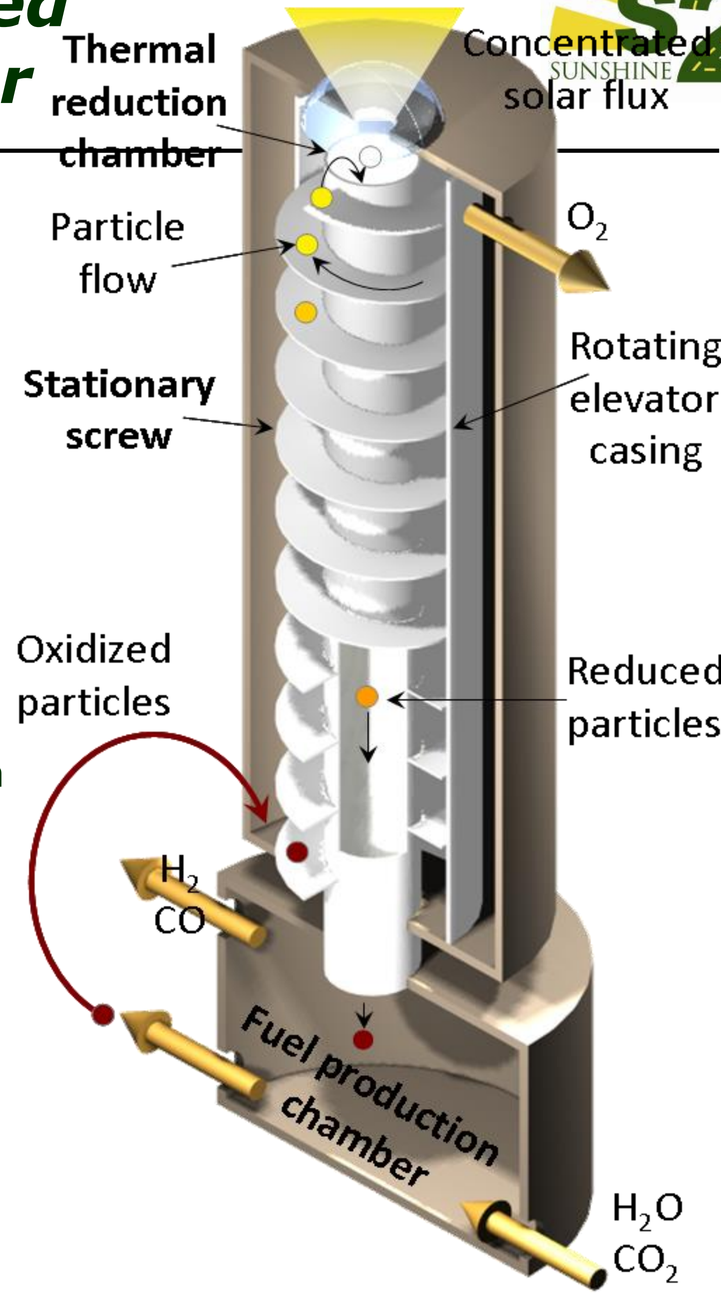




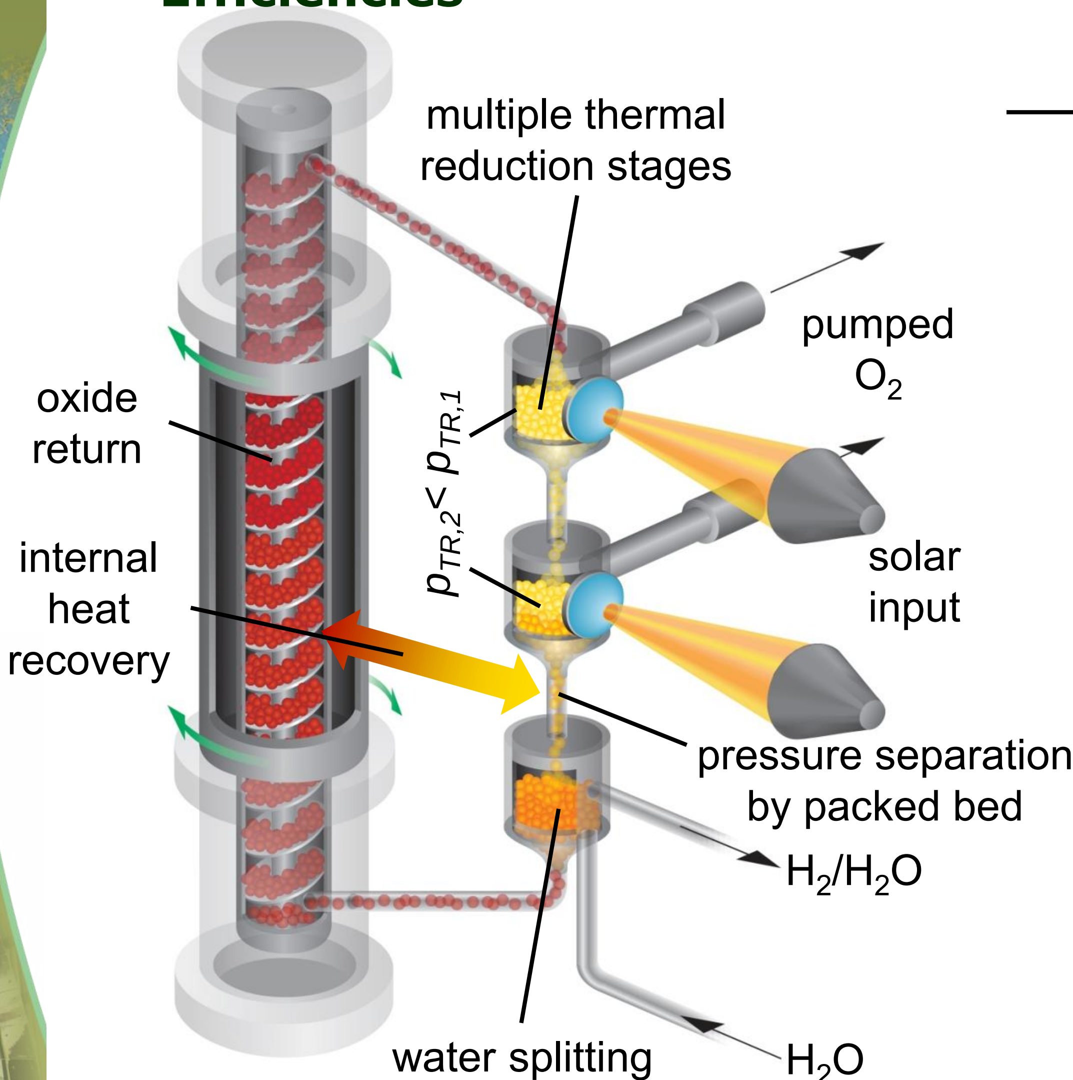
Generation 2: Packed Bed Particle Reactor

- **Direct solar absorption by the working material**
- **Sensible energy recovery between T_H and T_L**
- **Continuous on-sun operation**
- **Pressure, temperature and product separation**

- Pros:
  - Small reactive particles (~100mm)
  - Only particles are thermally cycled
  - Independent component optimization
  - Easy material replacement
- Cons:
  - Particle conveyance
  - Beam-down optics

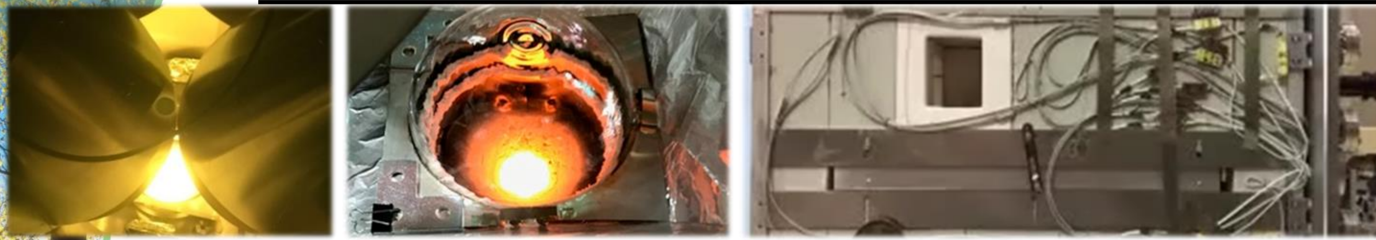


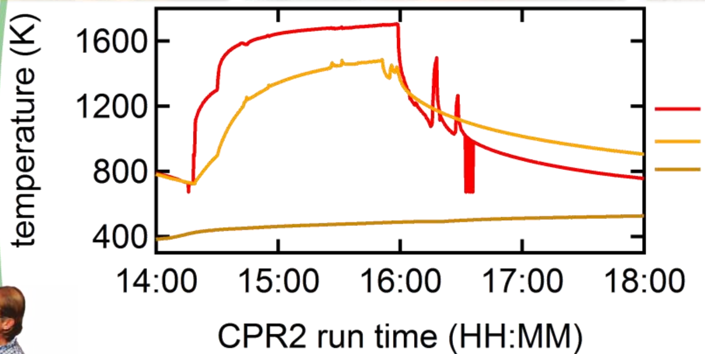
The Cascading Pressure Reactor Embodies the Packed Bed Reactor Design with Increased Efficiencies

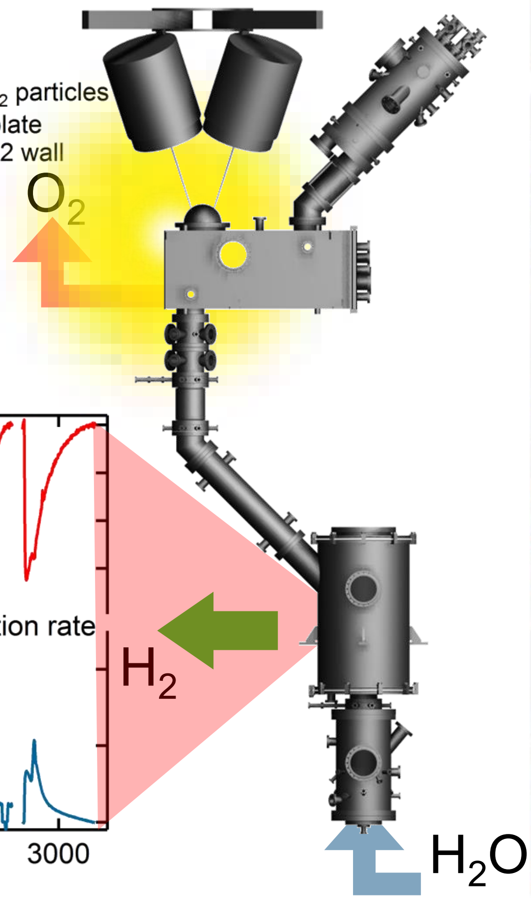


Incrementally pumping O_2 reduces the overall flow volume and velocity

We recently produced 2L of H_2 over 1 hour.

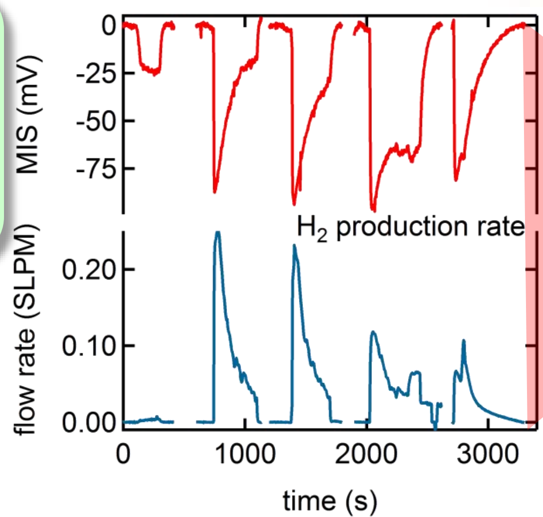


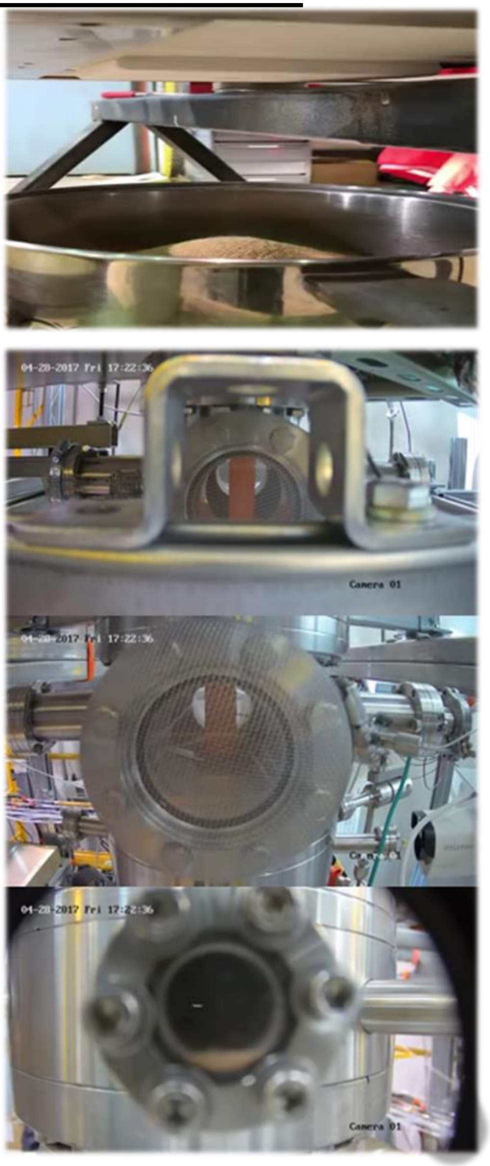




T_R~1700 K

0.25 SLPM peak H_2 rate

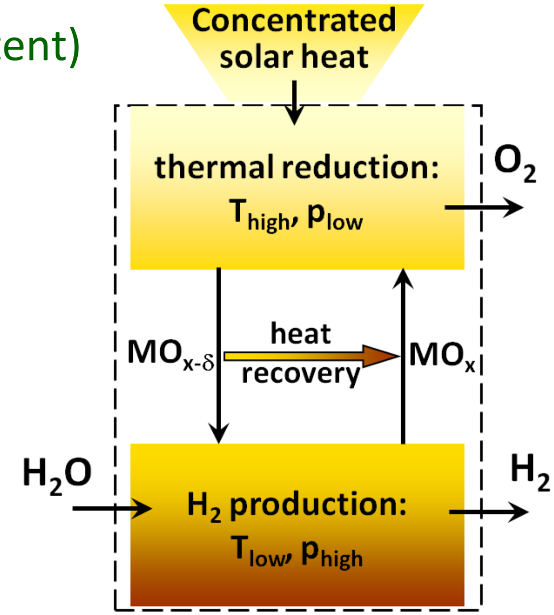




Sunshine to Petrol

Thermodynamics, kinetics, and stability are technological challenges for materials.

- Redox thermodynamics and kinetics.
  - Critical to reactor design and efficient operation
  - Large, reversible oxygen deficiency (reduction extent)
  - Fast redox rates and matched to solar flux
- Stability and long-term durability of redox active ceramic structures.
  - Cycle life ~ 300,000 cycles (10 year life)
    - heating rates (1000°C/min)
  - Compatibility with materials of construction
- Earth abundant and easy to manufacture.

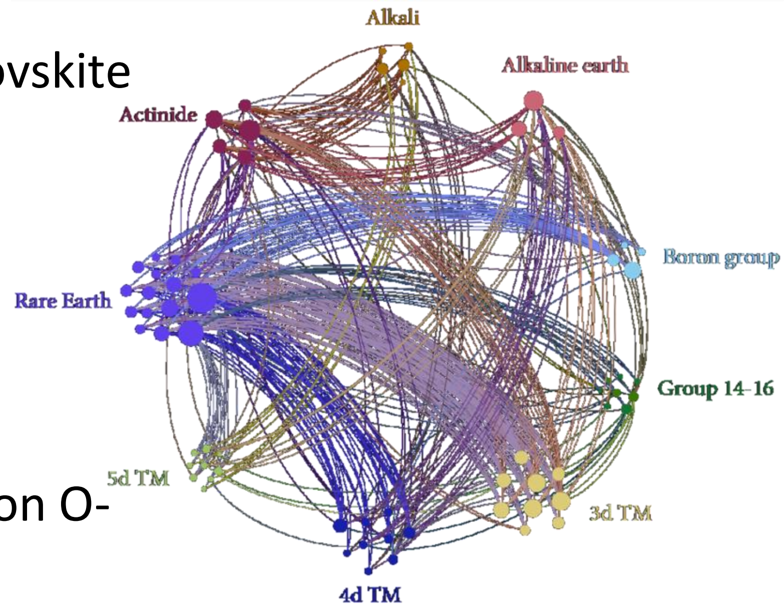


Two-step metal oxide cycle

Miller et. al, *Advanced Energy Materials* **2013**, DOI:10.1002/aenm.201300469

Predictive simulations (DFT) help design new materials formulations.

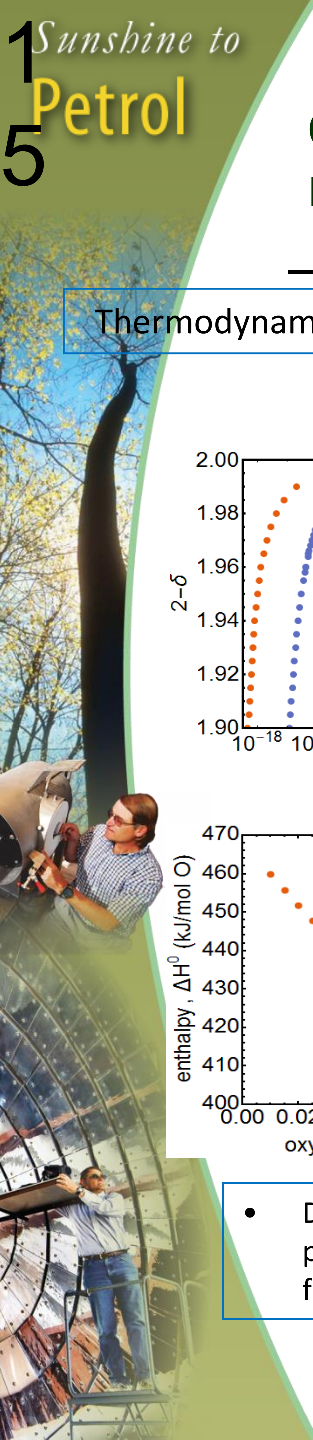
- 5,329 cubic and distorted perovskite ABO_3 compounds.
- Initial screening based on:
  - thermodynamic stability
  - $E_{f,O}$ = 2.5-5.0 eV
- Small (%) lattice expansion upon O-defect formation.
  - lattice softening ⇒ higher entropy
- Discard improbables.
  - Actinides, rare elements.



Evaluate the WS potential for remaining simple binary perovskites (~20)

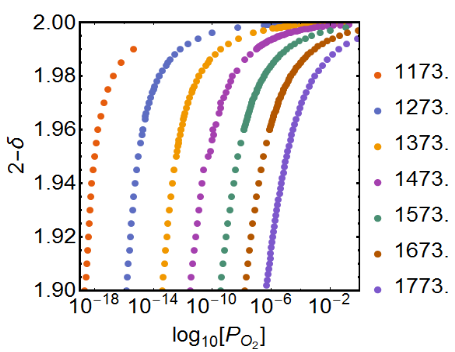
Formula	B-site
LaCoO3	Co
CeCoO3	Co
YCrO3	Cr
CeCrO3	Cr
LaCrO3	Cr
YFeO3	Fe
LaFeO3	Fe
CeFeO3	Fe
YMnO3	Mn
LaMnO3	Mn
CeMnO3	Mn
NaMoO3	Mo
SrSnO3	Sn
BaSnO3	Sn
CaVO3	V
SrVO3	V
YVO3	V
CeVO3	V
LaVO3	V

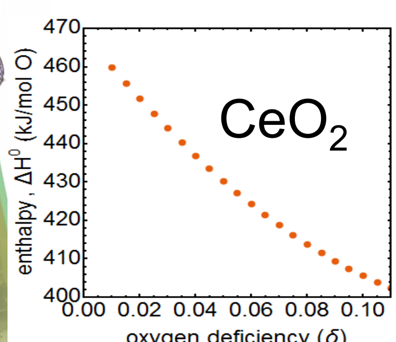
A. A. Emery, J. E. Saal, S. Kirklin, V. I. Hegde, C. Wolverton, *Chemistry of Materials*. **28**, 5621–5634 (2016).



Characterization helps design new materials formulations.

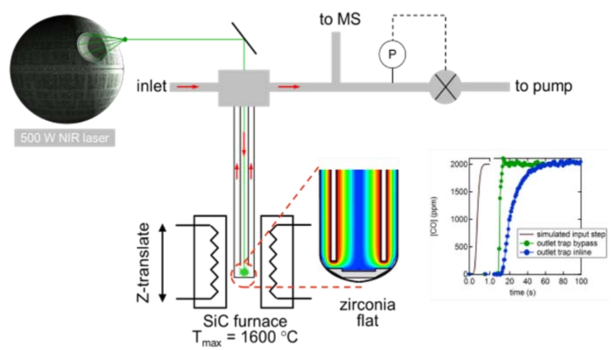
Thermodynamics: TGA and others

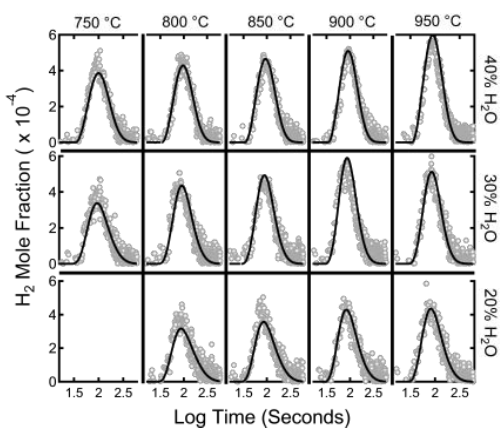




- Derive thermodynamic properties for material from P_{O2}-T-δ relation

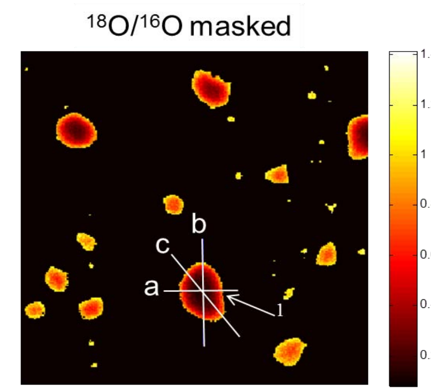
Kinetics: idealized flow reactor

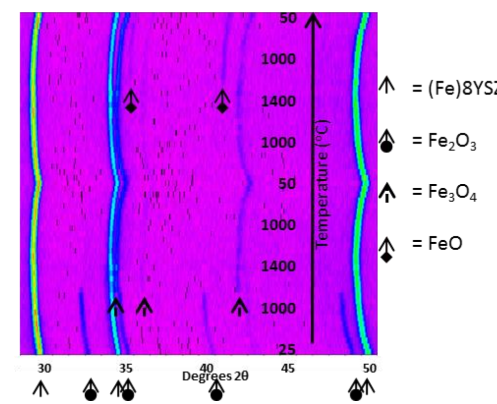




- Cycled under high radiative flux.

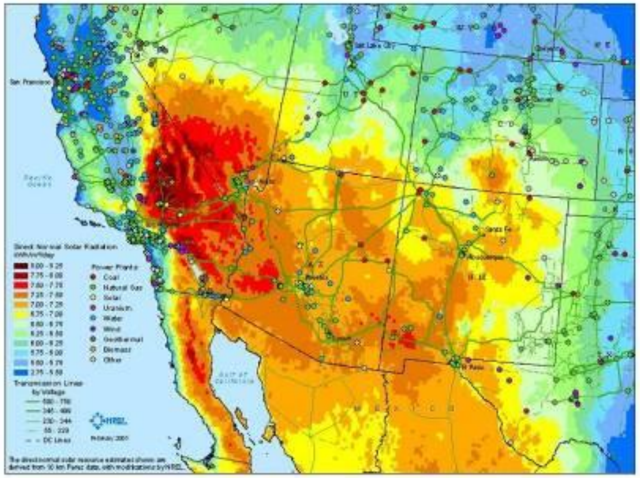
Structural: (i.e., HTXRD, ToF-SIMS)





- Great potential for operando X-ray scattering.

Solar Resources Analysis Shows the Promise of Scale and Requirement for High Efficiency Target



Filters applied (Resource analysis by NREL): Over-filtered

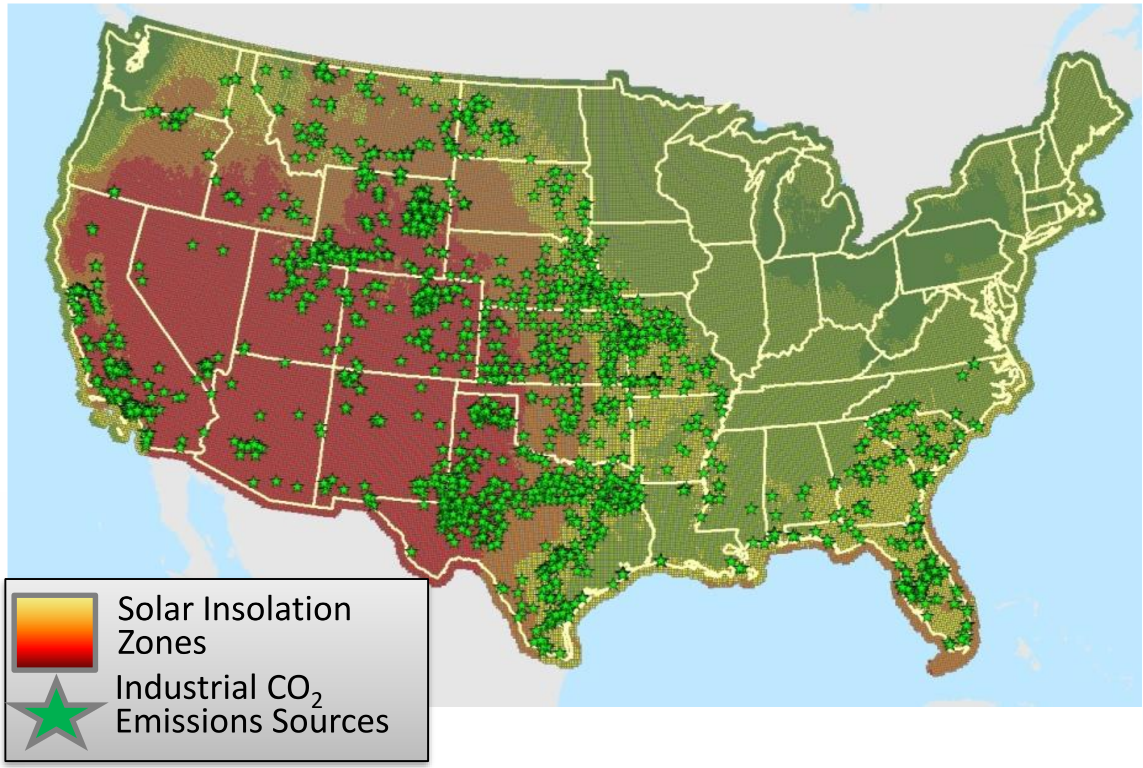
- Sites > 6.75 kwh/m^2/day
- Exclude environmentally sensitive lands, major urban areas, etc.
- Remove land with slope > 1%.
- Assume 25% packing density
- Only contiguous areas > 10 km^2 (675 MW$_{primary}$) 10 km^2 = 10^7 m^2 = 3.86 mi^2

State	Land Area (10^9 m^2)	Solar Capacity (TW)	Fuel Capacity (GW)	Fuel Capacity (mb/d)
AZ	49.9	3.37	421	5.9
CA	17.7	1.20	150	2.1
CO	5.5	0.37	46	0.7
NV	14.5	0.98	122	1.7
NM	39.3	2.65	331	4.7
TX	3.0	0.20	25	0.4
UT	9.2	0.62	78	1.1
Total	139.2	9.39	1,174	16.6

- U.S. Petroleum Demand is 20.7 mb/d (2007)
- **12.5%** lifecycle efficiency could produce 16.6 mb/d (**80%** of total U.S. demand)
- NM alone could produce **23%** of U.S. demand
- **12.5%** of available land (17.4 × 10^9 m^2) could provide **10%** of U.S. demand

139 billion m^2 is 1.5% of total U.S. land

Numerous Large CO_2 Sources Exist

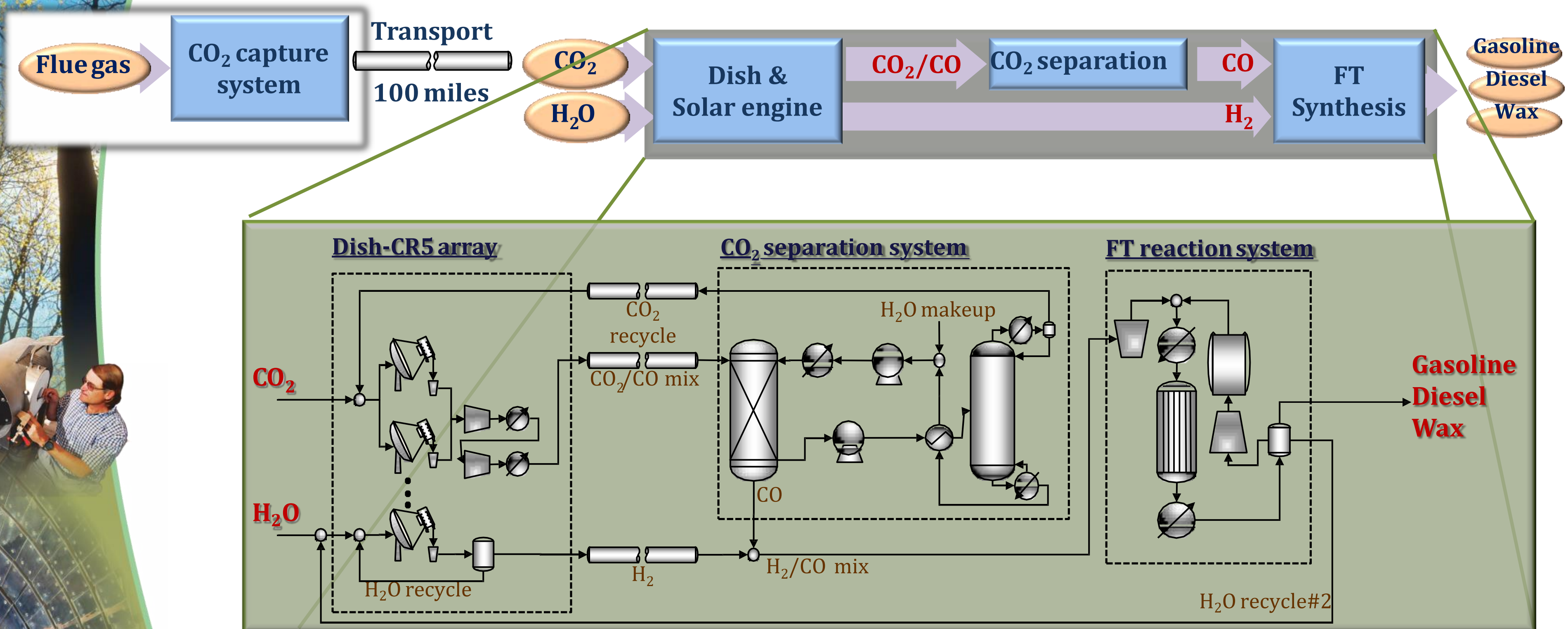


- Hundreds of large industrial CO_2 emissions sources exist in the United States in areas of high solar insolation.
  - 4-Corners Power Plant: 15.6 Mt/y and San Juan 13.4 Mt/y
  - At 81% utilization these two plants can supply fuel plants up to 9.8 GW (139 kb/d)
  - ~**25 plants** of comparable size to 4-Corners could supply US CO_2 for **10%** of U.S. demand.

Substantial resources can be tapped.
Infrastructure exists for CO_2 transport.

We Investigated a Number of Pathways and Products including MeOH and FT.

Mixed pathway to Fischer-Tropsch (FT) products



- Feed

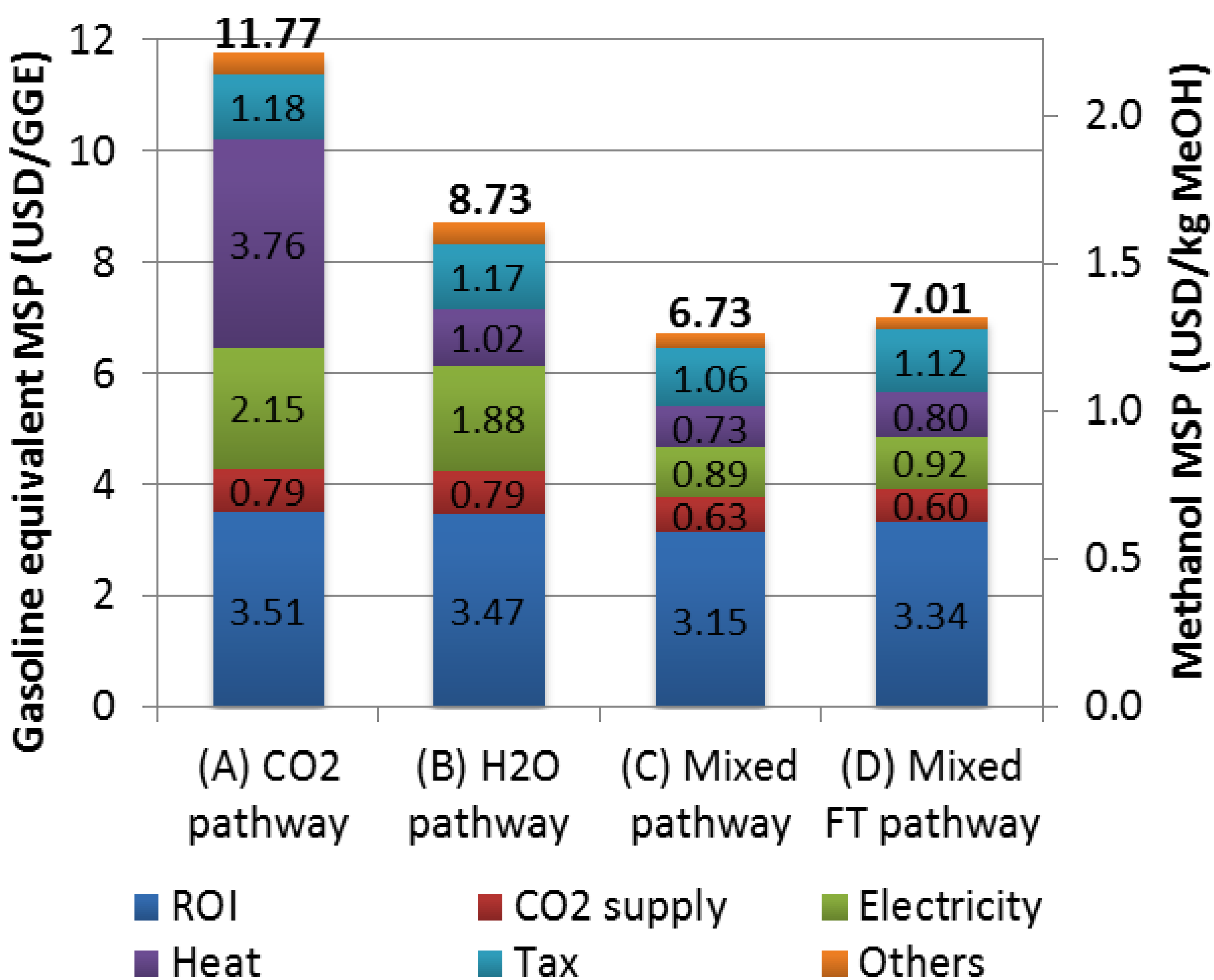
CO_2: 352 kmol/hr

H_2O: 395 kmol/hr

- Product

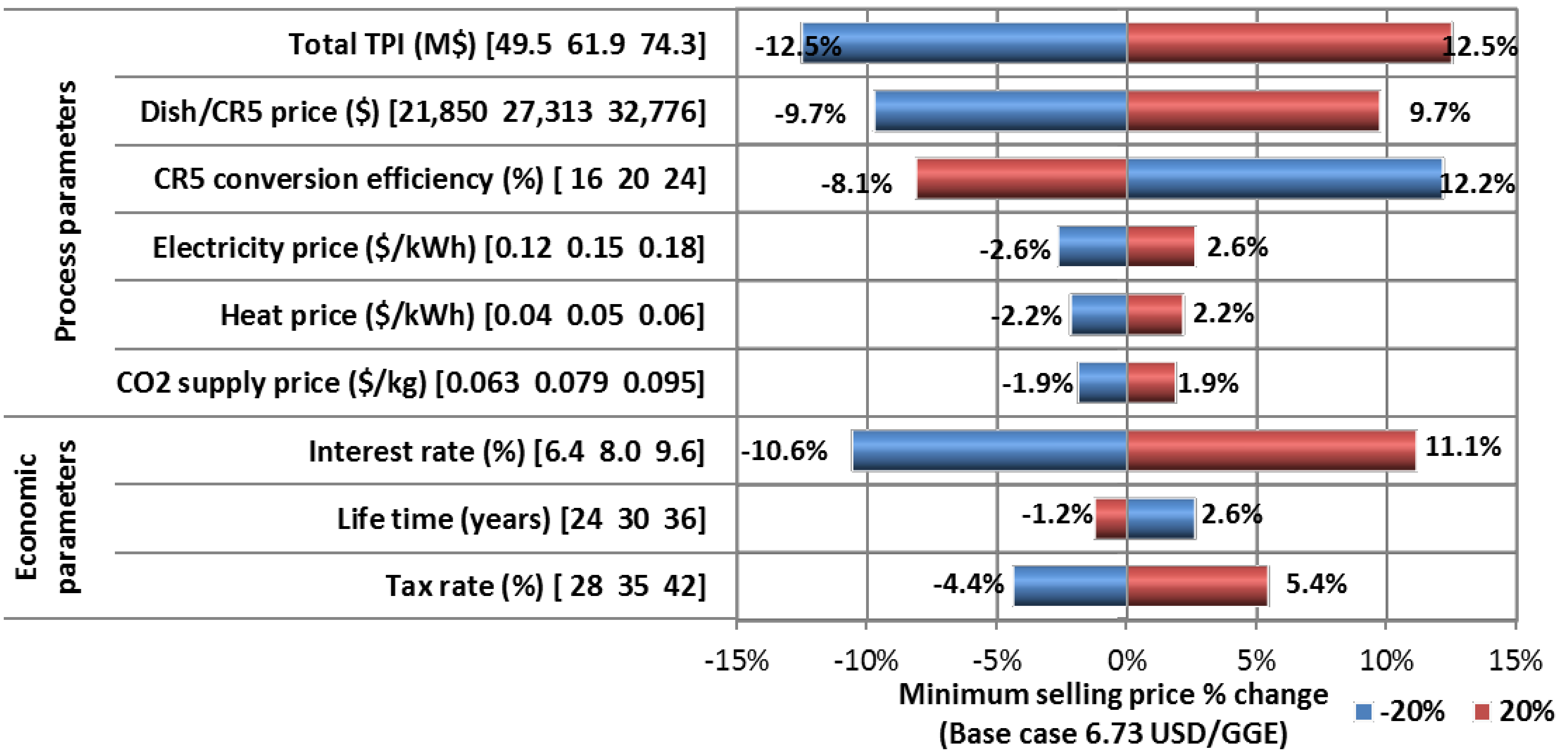
Gasoline (C7)/Diesel (C14)/Wax (C25): 24/10/1 kmol/hr (333 kmol C/hr)

Economic Evaluation: Minimum Selling Price



Economic Evaluation: Sensitivity Analysis

Mixed pathway to MeOH

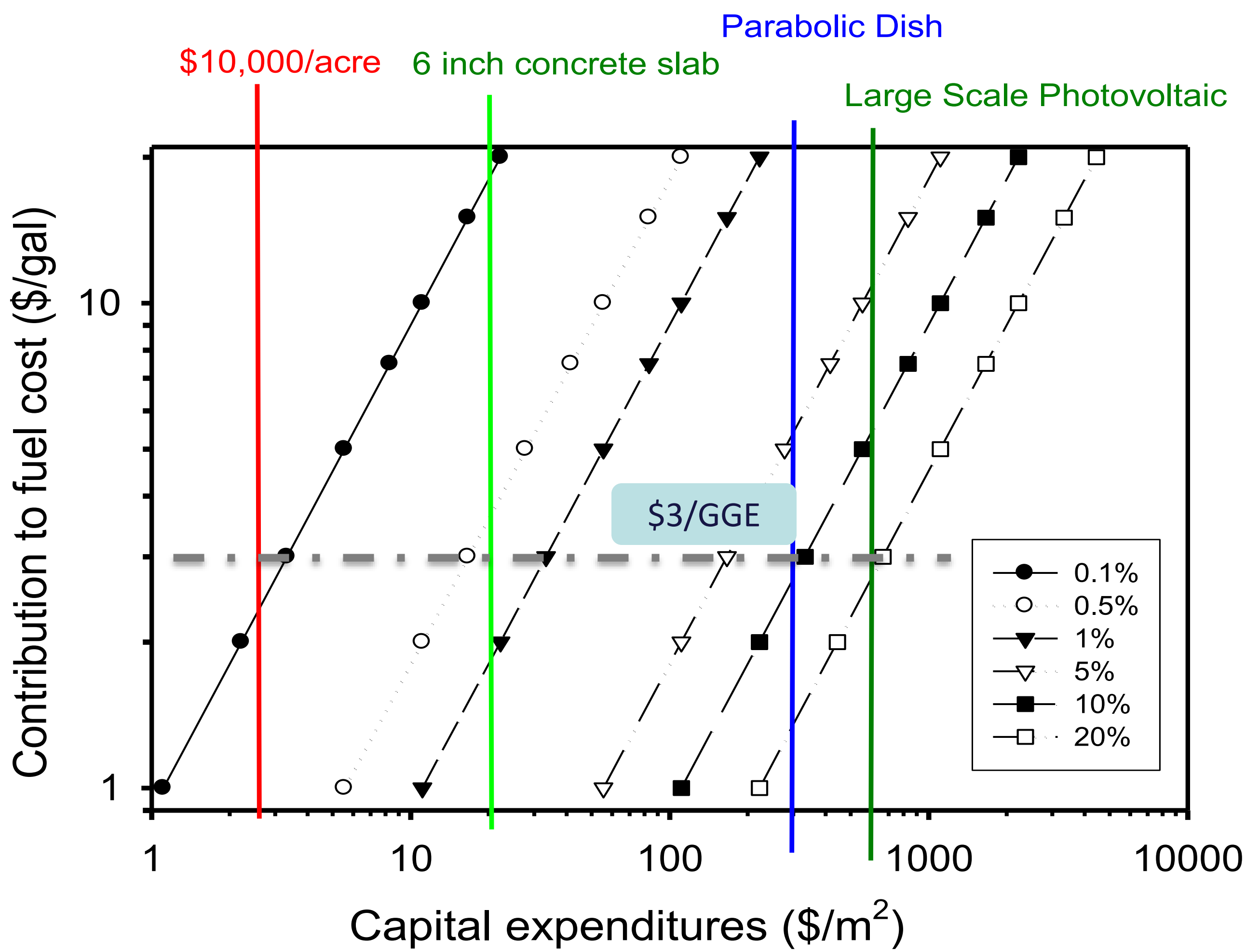


Technical Summary

- **Efficiency is key for cost and scalability**
  - Sunlight is the high cost feedstock (capital to capture)
  - Adjacency to other technologies (e.g. solar electric, solar reforming) offers benefits
- **High utilization is essential to achieving high efficiency**
  - Recuperation, reduction extent, kinetics
  - Need for new materials with optimized thermodynamics, transport properties, structures, physical properties, and thermally efficient reactors
- **Three aspects to advancing materials**
  - Improved compositions (modification and discovery)
  - Structuring materials
  - Integrating materials and reactor design
- **Production and testing of Gen1 CR5 completed; Gen 2 packed bed reactor tested**
  - Efficiency > 0.8%, Scales to > 1.5 %
  - Full-days of continuous on-sun testing at powers up to 9 kW.
  - Applying lessons to Gen2 designs and Materials


Thank You For
Your Attention

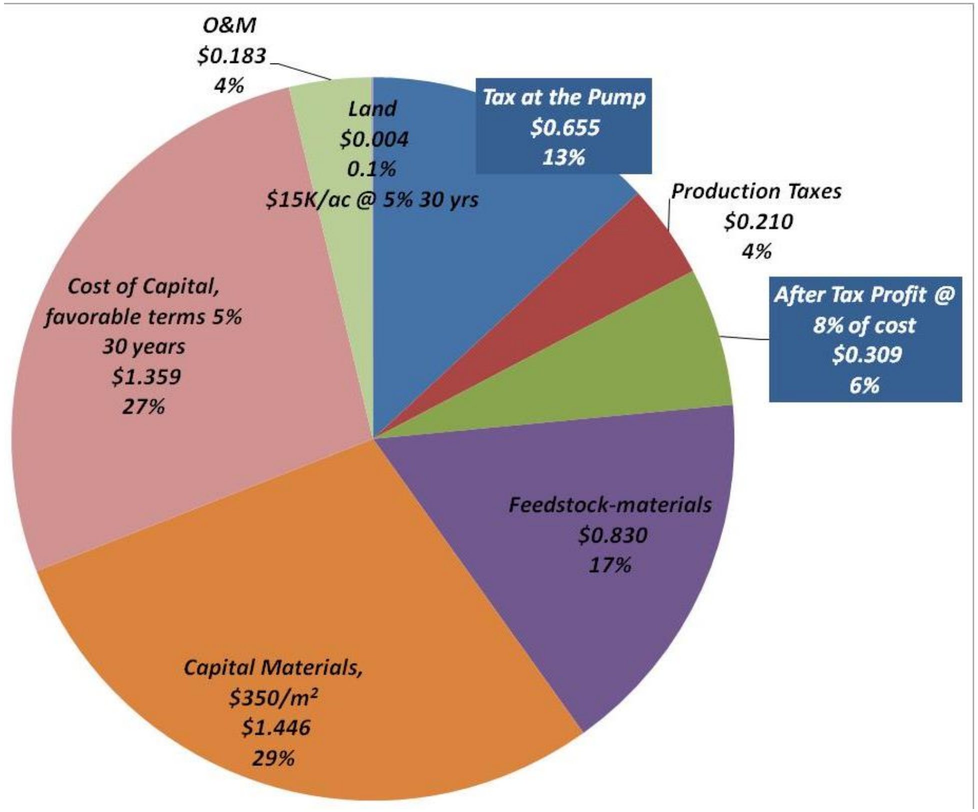
Efficiency → Costs: Collector Area



Assumptions: GGE = 36 kWh, Solar Resource = 2600 kWh/m²/yr, Favorable Financing (5% interest, 30 years)

Sunshine to Petrol

Cost Breakdown For $5/GGE; S2P 12.5% LCE



- **Costs for S2P are in the ballpark of viability**
- **Learning curve will reduce the most expensive contributions**
- **Very sensitive to the cost of capital recovery**